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Kh. Kh. Habibulloev^a; D. S. Saidov^a; S. L. Krapivskii^a; G. E. Zaikov^b

^a Tadjik State University, Dushanbe, Tadjik SSR, USSR ^b Institute of Chemical Physics, Moscow, USSR

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The Study of Oxygen Pressure Effect on Oxidation of Strained Elastomers

KH. KH. HABIBULLOEV, D. S. SAIDOV and S. L. KRAPIVSKII

Tadjik State University, Lenin Prospect, 17, Dushanbe, Tadjik SSR, USSR

and

G. E. ZAIKOV

Institute of Chemical Physics, Kosygin Str. 4, Moscow, 117334, USSR

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The oxygen pressure effect on the oxidation process of strained elastomers provides the experimentally observed complex pressure dependence of the process rate. Originally increasing the oxidation rate is then dropping with the increase of oxygen pressure from 30–730 mm Hg. The similar behaviour of the dependence is explained by the dual role of the pressure in the above process. The relation between the oxidation and the oxygen pressure is presented. The value of activation volume of $2.5 \times 10^4 - 2.5 \times 10^5$ cm³/mol obtained using the above relationship is explained by the activation zone theory. The increase of oxidation rate at P-const and fixed mobility of the molecules, relaxation times and the diffusion coefficient effected by stretching loads is explained by the volume activation dependence of the deformation. The computer simulation of the obtained relation is provided confirming all the experimentally observed pressure features of oxidation of strained and unstrained elastomers.

KEY WORDS Oxidation, elastomers, strain, oxygen pressure.

INTRODUCTION

A great deal of literature, concerning the effect of oxygen pressure on the oxidation process relates to solid vitrified polymers. According to literary sources two groups of pressure effects on the kinetics of the reaction can be distinguished.

The first group is the rate increase of both elementary stages and the oxidation process itself with the increase of small parameters of oxygen¹:

$$W_{O_2} = K_{er} [O_2] = K_{er} \cdot \gamma \cdot P_{O_2} \quad (1)$$

where γ is the Henry coefficient. The same paper provides the typical dependence showing an increase of oxidation rate of polypropilene with increasing pressures. The accelerating effect of the latter is shown for the addition of oxygen to alkyl radicals² to yield hydroperoxide³ and kill macroradicals.⁴

The effect of large ordinary hydrostatic pressures relates to the second group.

At omnilateral compression the pressure effects physico-chemical properties of polymers strongly decelerating the above processes.⁵ According to the concept of the activation character of the diffusion⁶ and chemical reaction⁷ the large pressure increases the work of activation volume V formation by PV , i.e., the increase of the activation energy occurs. This results in the decrease of the reaction rate and the diffusion coefficient:

$$K = K_0 \exp(-PV^*/RT) \quad (2)$$

$$D = D_0 \exp(-PV^*/RT), \quad (3)$$

as well as the increase of both relaxation times of molecular movements and correlation times^{8,9} exhibiting a decrease of the segmentary mobility in the polymer.

The analysis of the above factors provides the following general mechanism of the pressure effect on the kinetics of oxidation of polymers. The polymer oxidation is effected by two oppositely directed processes accelerating or decelerating the above process: 1. The increase of W_{O_2} with the small pressure increase of oxygen; 2. the decrease of chemical rates (including the oxidation) at high pressures of omnilateral compressions.

Data for the oxygen pressure effect on the oxidation of polymers being in specific highly elastic state are practically absent. Hence, the present paper relates to the study of oxygen pressure effect on elastomers. The samples were affected by both pressure variation and uniaxial stretching. The aim of the study is the investigation of the kinetics of oxidation of both strained and unstrained elastomers in pure oxygen and in the air under different pressures.

EXPERIMENTAL

Films of 50–150 mcm thickness were exposed to 30, 65, 105, 270 and 730 mm Hg of pure oxygen and at 30, 50, 65 and 165 mm Hg of atmospheric O_2 . The range of relative extensions was 0–400 percents. Unfilled vulcanizates of stereoregular commercial cis-1,4 polyisoprene (SCI-3) and butadienenitrile copolymer (SCN-40) vulcanized according to standard technique were investigated. Both purified in CCl_4 and raw materials were used. The oxidation was monitored according to the state of concentration of $C=O$ groups, defined by the position of the D/l 1740 cm^{-1} band of the IR spectra (D is the optical density of the band; l is thickness).

Spectrophotometer UR-20 and Specord 75 IR were used for IR spectra recordings. The oxidation was carried out in the diffusion mode. According to various sources^{10,11} the l_{CR} parameter being the boundary between the kinetic and the diffusion modes for rubbers equals to 2–50 mcm at atmospheric pressure. Being adequately aware of the difficulties of the correct specification of the diffusion-controlled process we nevertheless had to stick to the above mode so as to at least avoid its change with the 0 pressure increase.¹² If $l_{CR} = 2$ mcm is correct dealing with such thin films of elastomers so as to be within the kinetic mode its strongly difficult.

The experiments held showed that at smallest $P_{O_2} = 30$ mm Hg l_{CR} lies below

20 mm. The thicknesses used always exceeded 50 mm. As the process occurs in the diffusion mode at boundary experimental pressures it can be naturally supposed that the oxidation is the diffusion-controlled process within the total pressure region. This conclusion is confirmed by the observed W_{O_2} dependence of the film thickness for all oxygen pressures.

RESULTS

The experiments performed yielded a set of kinetic curves of oxidation for each predetermined P_{O_2} varying in magnitude of relative extension ϵ . Figure 1 is the typical picture at $P_{O_2} = 250$ mm Hg. The kinetic curve has a shape characteristic of the autocatalysis process stretching to the plateau. Stretching to the plateau occurs usually after 70 days of the process. Hence, the values after a 80-day period were chosen from $c(t)$ curves to obtain the dependence of rate increase of concentration of C=O groups on the oxygen pressure. Concentrations of carbonyl groups are presented in the reduced form $(D - D_0)/D_0$. They were taken at equal intervals of time at the saturation portion which allows to speak of the average process rate. Figure 2 is characterized by a complex dependence consisting of portions of increase and subsequent drop with increasing pressures. This dependence differs from Reference 1 for polypropylene. The complex shape of the curve is preserved for all strains. Hence, this phenomenon which may be called pressure inversion of the oxidation rate is exhibited irrespective of the extension of the rubber.

At the same time the strain of the sample results in the increase of the oxidation rate. This is revealed on the diagram as follows: the curve $W(P)$ lies lowest at ϵ

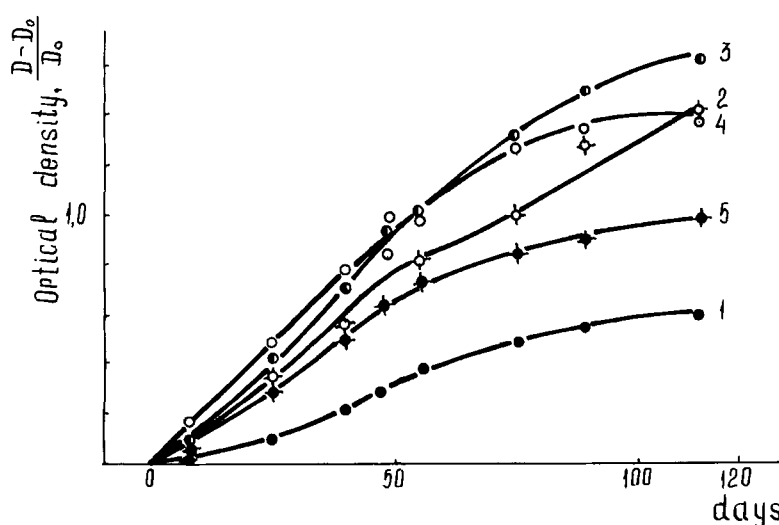


FIGURE 1 Concentration of C=O groups vs period of staying in pure O_2 at $P_{O_2} = 250$ mm Hg for SCI-3. Strain applied: (1) $\epsilon = 0\%$; (2) $\epsilon = 100\%$; (3) $\epsilon = 200\%$; (4) $\epsilon = 300\%$; (5) $\epsilon = 400\%$. Curves (1) and (2) refer to unpurified samples; (3)–(5) refer to purified samples.

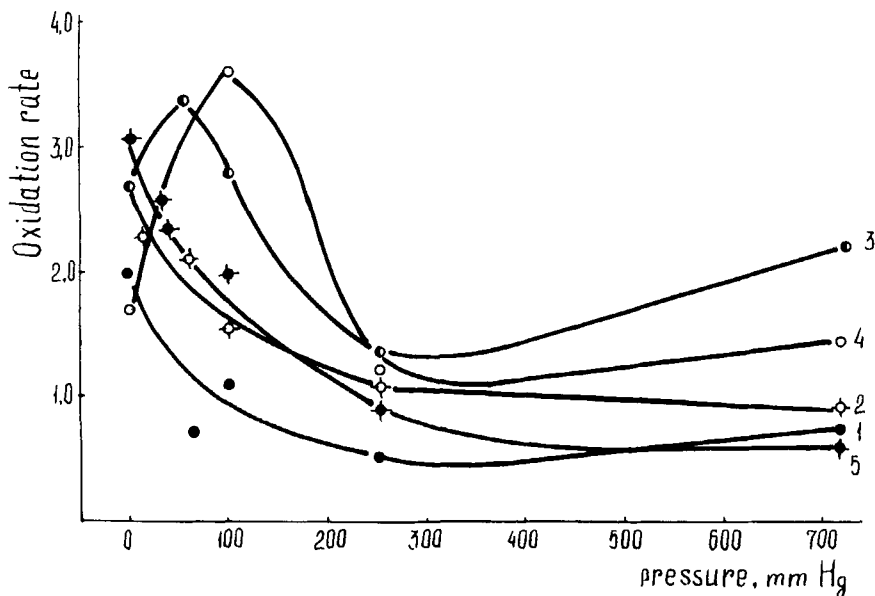


FIGURE 2 Rate of oxidation vs O_2 pressure. Numerization of curves is given according to Figure 1.

= 0, then with increase a successive arrangement of curves for $\epsilon = 100, 200$ and 300 percents is observed. The shape and the location of the $W(P)$ dependence at $\epsilon = 400$ percents lying differently will be explained below.

Of great interest is the maximum in the low P region which is the evidence of the fact that the process flow is effected by the opposing competing factors. The absence of the above maximum for samples characterized by relative extension less than 200 percents in the pressure range investigated is the evidence of the fact that such polymers have a maximum lying in the pressure range below 30 mm Hg. Naturally all graphs have to be in the extreme form as the oxidation rate has to approach to zero with the pressure decreasing to zero. This is naturally associated with the fact that the above process can not occur in the absence of oxygen. Judging by the sequence of the location of $W_{\max}(P)$ maximums for 200 - and 300 percents strained SCI-3 it can be concluded that the extension of the elastomer results in P_{\max} shift towards increasing pressures, shown in Figure 3. The next regularity observed in Figure 2 is the increase of maximum i.e., the increase of maximum oxidation rate $W_{\max}(P)$ with the sample orientation up to 300 percents. At the same time the polymer extension by 400 percents results in the deceleration of the oxidation process and moving the maximum back to the range of initial pressures not observed during the experiment. The SCI-3 as the crystallizing polymer is known to form a crystal phase in the strain range 350 percents. The growth of crystal regions with the small O_2 penetration complicates the oxidation process. Hence, the location of the curve and the maximum return effect are supposed to be associated with the variation of the elastomer structure due to its crystallization occurring at $\epsilon = 400$ percents. The form of the dependence of the oxidation rate decreases with the pressure was subsequently defined from left-hand branches of

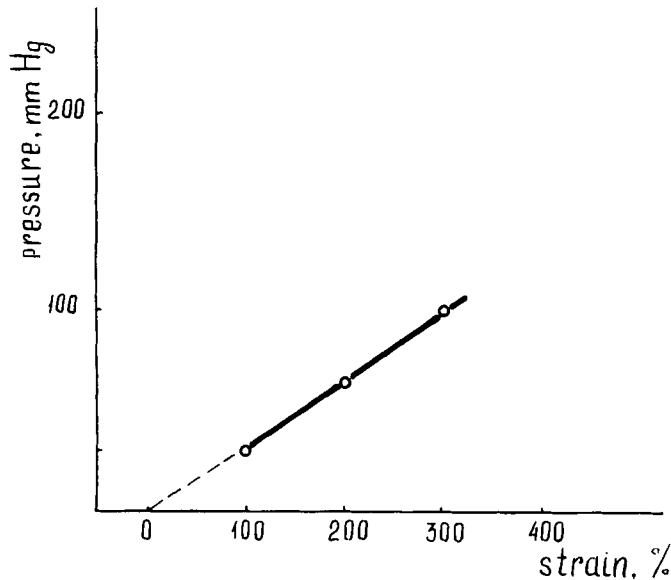


FIGURE 3 W_{O_2} shift with pressure vs strain. The dashed line shows the extrapolation for pressures below 30 mm Hg.

$W(P)$ curves presented in Figure 2. The linearity of semilogarithmic anamorphosis $\ln W(P)$ (Figure 4) proves the exponential drop of rate in the pressure range below 300 mm Hg:

$$W(P) \sim \exp(-\alpha P) \quad (4)$$

The presence of the point of inflection for $\ln W(P)$ results in the possible interference of some other processes, e.g., gas plasticization of the elastomer.¹³

The aspect of pressure inversion in the process of oxidation in the air presented some interest.¹⁴ Figure 5 presents experimental results of oxidation of unstrained and 100 percents strained SCI-3 and SCN-40. The dependence obtained in the pure O_2 is shown for comparison in the same figure (curve 1). The process is characterized by the W_{O_2} decrease with growing pressures which is still preserved in the air. At the same time the comparison of location of curves 1 and 2 shows that the process rate of samples placed in O_2 is 2–3 times that of samples placed in the air with similar oxygen content. The kinetics of concentration growth of $C=O$ groups of unstrained samples is too low being practically independent of the air pressure. The unstrained samples not effected by oxidation accelerating load weakly follow up the variation of even pure O_2 . These polymers are not capable of responding to the pressure variation in the air due to additional excess pressure of some other gases (N_2 , CO_2 , etc.) suppressing the oxidation process compared to pure oxygen. To check this version we performed an experiment on SCI-3 and SCN-40 (0- and 100 percents strained) in admixture of $O_2 + N_2$ as follows: the partial pressure P_{O_2} was 30 mm Hg, that of P_{N_2} 700 mm Hg. The experimental result is shown that the hypothesis of the decelerating effect of foreign gases seems to be justified. The

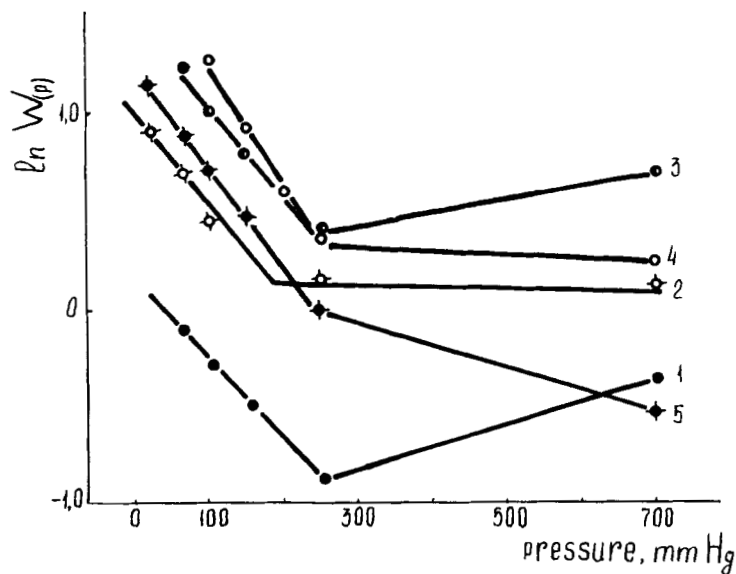


FIGURE 4 Semilogarithmic anamorphosis of $W(P)$ dependences for different strains ϵ .

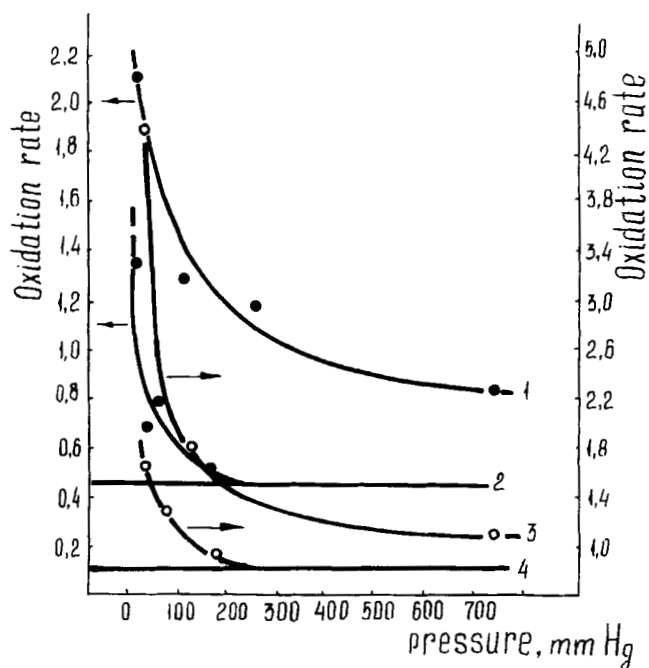


FIGURE 5 The rate of oxidation $W(P)$ dependence for SCI-3 (•) and SCN-40 (○); (1) and (3) in pure O_2 ; (2) and (4) in atmospheric O_2 ; (—•—) 100% strained samples; (—) unstrained samples.

rate of oxidation in admixture is really much lower compared to that in pure oxygen for both strains.

It's interesting to note that the similar experiment is given in Reference 15 for polystyrol. But the presence of N_2 in this case by no means effected the process rate.

The analysis of the dependences presented provides the following conclusions: 1. The increase of oxygen pressure results in a complex dependence of the oxidation rate of $W(P)$ on P_{O_2} : at pressures up to 100 mm Hg the oxidation rate increases and exponentially decreases on passing through the maximum. This phenomenon called pressure inversion is observed both in pure oxygen and in the air; 2. the oxidation rate of samples placed in pure oxygen is 2–3 times that of samples placed in the air with the same oxygen content; 3. the pressure inversion of the oxidation rate occurs within the total range of uniaxial extensions investigated; 4. the strain of the elastomer results in the shift of maximum towards the increase of oxygen pressure and in a simultaneous increase of maximum oxidation rate. W_{O_2} of unstrained samples is minimum.

DISCUSSION

The presence of the maximum for the dependence $W(P)$ supposes an interaction between competing factors and a dual role of the pressure. The oxidation rate is proportional to pressure in the range of initial pressures according to Equation (1). On passing the extremum P exponentially decelerates the oxidation process. Thus a possible superposition of oppositely directed processes mentioned in the introduction can be supposed. Really considering K to be proportional to the diffusion $K_{er} = AD$ in the diffusion mode (for reactants in a viscous isotropic media $K_{er} = 4\pi \cdot 10^{-3} \cdot N_A \rho D$ and combining Equations (1) and (2) yields:

$$W(P) = AD_0\gamma P_{O_2} \exp(-PV^*/RT)$$

This expression can be obtained in an alternative way. The diffusion-controlled oxidation is known to flow with the rate¹:

$$W_{O_2} = \gamma \cdot l^{-1} \cdot P_{O_2} \sqrt{KD}$$

Hence, according to Equations (2) and (3) we obtain:

$$W(P) = \gamma \cdot l^{-1} \cdot A \cdot P_{O_2} \sqrt{K_0 D_0} \exp(-PV^*/RT) \quad (5)$$

The analysis of both dependences really shows a maximum for $W(P)$ at pressure:

$$P_{\max} = \frac{RT}{V^*} \quad (6)$$

From Equation (5) the maximum oxidation rate in P_{\max} is obtained:

$$W_{\max} = A\gamma P_{O_2} \sqrt{K_0 D_0} / e1 = A\gamma \sqrt{K_0 D_0} RT / eV^*1, \quad (7)$$

where $e = 2,71 \dots W_{\max}$ is seen to be proportional to the oxygen pressure and, hence, to its quantity dissolved in the sample according to Equation (1). Expressing Equation (6) in terms:

$$V^* = \frac{RT}{P_{\max}} \quad (8)$$

the activation volume V^* can be evaluated, which is the effective value in this case related to oxygen diffusion. The above experimental value is of the order $V^* = 2,5 \times 10^5 \text{ cm}^3/\text{mol}$ at $P = 65 = \text{mm Hg}$ and $= 200$ percents. The calculation of the activation volume at atmospheric pressure by substituting $P = 1$ in Equation (8) (which is not quite correct due to the absence of the maximum in this region) provides $V^* = 2,5 \times 10^4 \text{ cm}^3/\text{mol}$. The same result is obtained by using modified pressure dependences in which subexponential expressions take the form¹⁶:

$$\frac{PV^*K_0}{RTK} \quad \text{and} \quad \frac{PV^*}{KV_0}$$

where V_0 is the elementary fluctuation volume at $P \rightarrow 0$; K is the volume modulus of elasticity and K_0 is the volume modulus of elasticity at $P \rightarrow 0$.

These significant values of activation volume are in contradiction to the literature. It is generally accepted that the activation α - relaxation volume of the vitrification process with $V^* = 5 \times 10^2 \text{ cm}^3/\text{mol}$ ¹⁷ is the largest due to macromolecular segments participation in this process. The exception are anomalously large V^* calculated from the structure-sensitive coefficient for SCI-3¹⁸ of Zhurkow equation.¹⁹ Still the exception are recently published data²⁰ for activation volume of elastomer creepage, where $V^* = 3 \times 10^4 \text{ cm}^3/\text{mol}$. This value is two orders of magnitude that of the similar one for vitrification process being excellently correlated with the obtained value of V^* .

This situation can be explained within the activation-zone theory.²¹ This theory suggests that in the diffusion process two neighboring sections of polymer chains including several segments must be separated by the distance adequate for molecular passage. This state of polymer matrix microsection demands for some energy to be expended and is the activated one. It is noticed in Reference 22 where most theories of activation zones are summarized that the elementary diffusion effect in elastomers is to be necessarily associated with the presence of the significant activation zone. It's interesting to note that the creation of the above theory is brought up by the disagreement in two orders of magnitude calculated from experimental diffusion data on molecular hopping d-d distance of low-molecular matter being equal to molecular dimensions. This situation is similar to ours. In Reference 23 the hole model of diffusion in the polymer is presented considering intramolecular interaction of molecular segments. The estimations show that from 6 to 20 segments

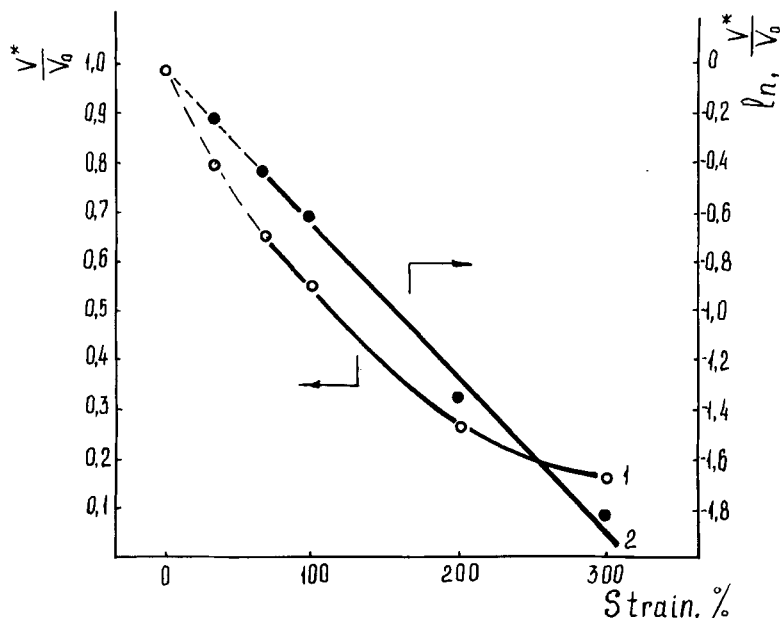


FIGURE 6 V^*/V_0^* (1) and $\ln V^*/V_0^*$ (2) vs strain of the sample. The value of V is obtained at $\epsilon = 0$. The dashed line shows the extrapolation for pressure below 30 mm Hg.

are shifted at O_2 diffusion in various polymer materials. As the volume $V^* = (300-550)$ cm^3/mol is associated with separate segments participating in the relaxation process¹⁸ a 10-fold increase in number of segments yields a 3 order of magnitude increase of the activation diffusion volume $V^* = (300-550) 10^3$ cm^3/mol . This is in excellent agreement with the obtained value of V^* .

Returning to Figure 3 note that P_{max} being shifted as the strain increase, i.e., each value of corresponds to its own value of extreme pressure $P_{max}(\epsilon)$, then substituting the latter in Equation (8) yields the variation of V^* with ϵ . The dependence takes the form:

$$V^*(\epsilon) = V_0^* \exp(-a\epsilon) \quad (9)$$

with the exponential change of activation volume with the extension of the elastomer (Figure 6). The value $\ln(V^*/V_0^*)$ lies satisfactorily on the straight line which confirms the correctness of the approach used. This form of the dependence is evidenced by curves in Reference 20 providing the dependence of the activation volume V^* of creepage on the degree of elastomer extension. The semilogarithmic anamorphosis $\ln V^* = f(\epsilon)$ also presents the straight line. The decrease of decline of straight lines in $W(P)$ is explained by Equation (9), since according to Equations (4) and (5):

$$\alpha = \frac{V_0^*}{RT} \exp(-a\epsilon)$$

Now let's return to Equation (5). Substitution of Equation (9) to Equation (5) yields the generalized dependence of the rate of oxidation for elastomers at cooperative effect of oxygen pressure and the strain. It can be conveniently rewritten in the form:

$$W(P, \varepsilon) = A' \gamma 1^{-1} P_{O_2} \exp[(-PV'_0 \exp(-\alpha\varepsilon))/RT] \quad (10)$$

At $\varepsilon = 0$ it acquires the form of Equation (5), while at constant pressure ($P = \text{const}$) the oxidation rate is modified by the strain of the sample. From Equation (10) it can be seen that $W(P, \varepsilon)$ increases with increase similar to W_{max} according to Equation (7). This phenomenon was really experimentally observed (Figure 2).

To test the working capacity and fitness to the experimental generalized dependence of Equation (10) the computer simulation was carried out. Selecting parameters in Equation (10) are varying pressure and relative extension all the experimentally observed pressure features of oxidation of oriented and disoriented elastomers were obtained. It shows both the presence of the maximum for $W(P, \varepsilon)$ and its shift with the simultaneous increase of the maximum oxidation rate at sample strain coupled with the exponential decrease of $W(P, \varepsilon)$ with the pressure increase. The increase of the process rate at $P = \text{const}$ and fixed molecular mobility of ($\tau^c = \text{const}$), relaxation time τ^R and diffusion D of rubbers affected by stretching tensions^{9,24,25} is explained here by activation volume dependence of V^* . The difference in oxidation rates of samples placed in pure oxygen and those in the air with similar O_2 content is also explained. The value of P in the preexponential expression slightly differs from that in the subexponent in Equation (3). P_{O_2} is strictly the partial oxygen pressure, modifying the quantity of O_2 dissolved in the sample according to $[O_2] = \gamma P_{O_2}$ while that in the subexponent is the total pressure. For oxidation in the air P_{O_2} doesn't equal to P hence, the process rate for the former case is below that in the pure oxygen.

Thus all experimental results obtained are based on the generalized Equation (10) presented. It can be supposed that the dependence of oxidation rate for elastomers on O_2 pressure and strain is obtained which is confirmed by experiments and computer simulation.

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